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(57) Abstract

A non polluting additive or spotting fluid which releases and/or prevents differentially stuck drill strings and casings in the wellbore of a subterranean well is presented. This additive composition comprises an ester, preferably monohydric alcohol esters of fatty acids in combination with particulate asphalt. A preferred ester is 2-ethylhexanol ester of a tall oil fatty acid. A preferred asphalt is the asphalt described in Patent 5,120,708. Other preferred components in addition to the ester and asphalt include one or more suitable surfactants, suspension agents such as lime ($Ca(OH)_2$), anticaking and grinding agent such as calcium silicate and antigellation agents such as sodium bicarbonate. The present invention enhances the lubricity of a drilling fluid to prevent drill string sticking and when utilized as a spotting agent reduces the time required to release a stuck pipe. By eliminating the need for oil-based components, the present invention is non-toxic to marine life, environmentally acceptable, easy to prepare, and capable of being disposed of at the drill site without costly disposal procedures.

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SPOTTING FLUID AND LUBRICANT

Background of the Invention:

This invention relates generally to a spotting fluid and method for dislodging a stuck drill string or casing during downhole drilling operations, and more particularly to an aqueous-based spotting fluid and lubricant comprised of an ester, preferably monohydric alcohol esters of fatty acids in combination with a water dispersable particulate asphalt.

During drilling operations the drill string may become stuck and cannot be raised, lowered, or rotated. One mechanism for causing this problem is known as differential sticking.

Differential sticking may be defined as the sticking of the drill string against a permeable formation containing less pore fluid pressure than the hydrostatic pressure exerted by the drilling fluid column and usually occurs when the drill string remains motionless for a period of time. The mechanism by which this occurs involves the drill string coming into contact with the permeable zone, remaining quiescent for a period of time sufficient for mud cake to build up on each side of the point of contact, thus sealing the pipe against the borehole. The annular pressure exerted by the drilling fluid then holds the pipe against the borehole or the permeable zone.

Freeing of differentially stuck pipe is essentially a matter of reducing this pressure differential which exists across the pipe. One method used simply involves a reduction in fluid pressure by replacing the annular fluid with a less dense fluid allowing for less pressure differential to exist between the borehole and annulus. In some cases the borehole pressure may exceed the annular pressure which in turn allows the pipe to be blown away from the borehole.

One commonly used method to release stuck pipe is the use of a "spotting" fluid in the hole opposite the stuck interval. The spotting fluid may penetrate between the mud cake and pipe lubricating the area between the pipe

and borehole resulting in less friction and quicker release. More often than not, an extensive period of time is necessary for this to occur which results in an expensive loss of rig time.

As mentioned above, spotting fluids were developed to lubricate the affected area, "spotting" referring to the placement of a quantity of drilling fluid known as a pill or slug containing a release agent at the area of concern. Furthermore, incorporating a lubricating agent into the drilling mud during ordinary operation to prevent drill pipe sticking is a common practice.

The composition of these release agents has generally consisted of various kinds of oils such as synthetic oils, vegetable oils, mineral oils, diesel oils and crude oils. Oil-based spotting fluids, however, are generally difficult to prepare because strong agitation is required to achieve an oil-water suspension taking much time when time may be a crucial consideration.

Disposal of drilling fluids containing oil components has also come under much closer environmental scrutiny and regulation concurrent with increasing concern about reducing pollutants in ground water and coastal water environs. Drilling muds containing oil are generally classified as pollutant streams having costly regulated disposal procedures. Such oils are not in the best interest of marine wild life and may leave an unsightly sheen in the water.

Accordingly, there is an urgent need for a spotting fluid release agent and lubricant in the art of oil and gas production which is nontoxic, non-oil based, inexpensive and easy to prepare and use.

Examples of non-oil based spotting fluids and lubricants proposed are found in U.S. Patent Nos. 4,964,615; 5,002,672; 5,127,475; 4,230,587; 4,466,486; 4,494,610; 4,614,235; and 4,659,486. Patent 4,964,615 to Mueller et al describes a composition for freeing jammed drill strings and pipes which utilizes a fatty acid alkyl ester or mixtures of esters as well as at least one thickener and at least one emulsifier. In a preferred embodiment, the Mueller et

al patent describes the use of ester of olec acid with 2-ethyl hexanol as a preferred fatty acid alkyl ester for use in the spotting fluid described therein.

Patent Nos. 5,002,672 and 5,127,475 to Hayes et al both describe an aqueous-based spotting fluid composition which utilizes a glycerophosphoric acid ester and a diacetyltartaric acid ester of mono and/or diglycerides. U.S. Patent 4,230,587 to Walker discloses a stuck drill pipe spotting fluid comprising polyethylene glycol while the Walker patent 4,466,486 utilizes a stuck drill pipe spotting fluid comprising a polymer (cellulose or polyethylene oxide). The Walker patent 4,494,610 utilizes an alcohol based spotting fluid while patent 4,614,235 to Keener et al is an ether based spotting fluid. U.S. Patent 4,659,486 to Harmon discloses a polyester based drilling fluid.

One notably successful attempt at overcoming the deficiencies of the prior art is the water-based drilling fluid additive composition sold by Milpark Drilling Fluids of Houston, Texas under the trademark AQUA MAGIC, the composition of which is described in detail in U.S. Patent 5,120,708, assigned to the assignee hereof and fully incorporated herein by reference. The drilling fluids additive of Patent 5,120,708 comprises (a) a water soluble polyoxyalkylene compound selected from polyoxyalkylene glycols, monoalkylethers of polyoxyalkylene glycols, and mixtures thereof in combination with (b) a water dispersible particulate asphalt. While well suited for its intended purposes, this composition is designed for prevention of sticking problems as opposed to correction of the sticking problem after the fact. Thus, there continues to be a need for an improved water-based spotting and/or lubricating fluid for alleviating and/or preventing differentially stuck drill pipe and casing.

Summary of the Invention:

The above-discussed and other drawbacks and deficiencies of the prior art are overcome or alleviated by the non polluting additive or spotting fluid of

the present invention which releases and/or prevents differentially stuck drill strings and casings in the wellbore of a subterranean well. This additive composition comprises an ester, preferably monohydric alcohol esters of fatty acids in combination with particulate asphalt. A preferred ester is 2-ethylhexanol ester of a tall oil fatty acid. A preferred asphalt is similar to the asphalt described in Patent 5,120,708. Other preferred components in addition to the ester and asphalt include one or more suitable surfactants, alkalinity control agents such as lime ($Ca(OH)_2$), water or aqueous solutions anticaking and/or grinding agents such as calcium silicate and antigelletion agents such as sodium bicarbonate.

In one embodiment, the present invention comprises a spotting fluid concentrate composition suitable for use in downhole drilling operations in a pill for releasing periodically stuck drill string. The concentrate comprises the novel combination of ester and asphalt described above together with the remaining optional surfactants, suspension agents, anticaking and grinding agents and antigellation agents.

In another embodiment, the present invention is a pill composition comprising the spotting fluid concentrate and a weighting agent for adjusting the density of the concentrate. The concentrate comprising an aqueous dispersion and/or solution of the novel combination of ester and asphalt described above together with the remaining optional surfactants, alkalinity control agents, water or aqueous solutions, anticaking and grinding agents and antigellation agents.

In a further embodiment, the present invention comprises a method for lubricating a downhole well drilling operation comprising the steps of: mixing a spotting fluid concentrate with a drilling mud and circulating the mud mixture through the well. The concentrate comprising an aqueous dispersion and/or solution of the novel combination of ester and asphalt described above together with the remaining optional surfactants, alkalinity control agents, water or

aqueous solutions, anticaking and grinding agents and antigellation agents. The drilling mud comprises the concentrate in an amount of from about 1 to about 25 percent by volume of the drilling mud, preferably from about 1 to about 10 percent by volume of the drilling mud.

In yet another embodiment, the present invention comprises a method for mixing a spotting fluid pill, comprising the steps of: mixing a suitable ester (e.g., monohydric alcohol esters of fatty acids) with an asphalt and optional surfactants, alkalinity control agents, water or aqueous solutions, anticaking and grinding agents and antigellation agents and conditioning the dispersion/solution with a weighting agent.

In yet a further embodiment, the present invention includes a method for releasing a stuck drill assembly in a downhole well drilling operation comprising the steps of preparing a pill of a spotting fluid composition; displacing a drilling fluid in the well with the pill in an amount sufficient to contact the well bore with the pill adjacent the location of the sticking; displacing the drilling fluid with an additional quantity of the pill until the drill assembly is free to move; and circulating the drilling fluid to incorporate the pill into the fluid. The pill composition comprises the novel combination of ester and asphalt described above together with the remaining optional surfactants, alkalinity control agents, water or aqueous solution, anticaking and grinding agents and antigellation agents and a weighting agent. The method may also include vertically working the drill assembly during the initial displacing step; and further removing the drill assembly prior to the circulating step and staging back into the well with the freed drill assembly.

The present invention thus enhances the lubricity of a drilling fluid to prevent drill string sticking and when utilized as a spotting agent reduces the time require to release a stuck pipe. By eliminating the need for oil-based components, the present invention is non-toxic to marine life, environmentally

acceptable, easy to prepare, and capable of being disposed of at the drill site without costly disposal procedures.

It will be appreciated that while it has been known to use esters in a spotting fluid or lubricant (e.g., Patent 4,964,615 to Mueller et al.), the inventors herein are unaware of any suggestion for the novel combination of ester and asphalt to provide the non-toxic, biodegradable and environmentally acceptable spotting fluid and lubricant of the present invention.

The above-discussed and other features and advantages of the present invention will be appreciated and understood by those skilled in the art from the following detailed description and drawings.

Description of the Preferred Embodiment:

The present invention discloses a spotting fluid composition free from mineral oils for freeing jammed drill strings and casings, comprising the novel combination of an (1) ester based fluid and (2) an asphalt. In addition, the spotting fluid composition may include one or more of surfactants, alkalinity control agents, anticaking agents, grinding agents, water or aqueous solutions, suspension agents and antigelling agents.

The ester used in the composition of this invention may generally comprise any oil soluble ester which is pumpable at room temperature. Monhydric alcohol esters of fatty acids (such as tall oil fatty acid esters) are preferred due to their low cost and resistance to saponification. Such esters are water insoluble, low viscosity, relatively stable to hydrolysis and exhibit a high flash point. A particularly preferred tall oil fatty acid ester is the 2-ethylhexanol ester of tall oil fatty acid which is commercially available, for example, from Arizona Chemical of Panama City, Florida under the designation ARIZONA 2154. Other examples of suitable esters include one or more liquid esters made from C_1-C_{10} alcohol esters of C_{12}-C_{22} saturated and unsaturated fatty acids,

namely, methyl, ethyl, proply, butyl, pentyl, hexyl, heptyl, 2-EH or isooctyl caproate, caprylate, laurate, myristic, palmitate, stearate, olenate, erucate or mixtures thereof.

The asphalt used in the composition of this invention may comprise any particulate asphalt. The asphalt may comprise any natural occurring asphalt such as asphaltites (e.g., gilsonite) and synthetic asphalts. A particularly preferred asphalt is disclosed in aforementioned U.S. Patent 5,120,708 and has an ASTM D-36 softening point of at least 290°F, an ASTM D-5 penetration depth not exceeding 5 mm. and a particulate size not exceeding more than 10 percent retained on a 2 mesh screen.

The ASTM test methods may be found in the annual book of ASTM Standards, Part 15, The American Society for Testing and Materials, Philadelphia, 1979: Test D-36 at pages 107-110, and Test D-5 at pages 88-92.

Such an asphalt can be prepared by oxidizing asphaltic residuum from naphthenic crude at temperatures in the range from about 450°- 500° F for from about 6 to about 10 hours. The oxidized hardened asphalt is pulverized to a mesh size of not more than about 10 percent retained on a 40 mesh U.S. screen. Oxidized asphalt having a penetration depth in the range from about 6 mm to 10 mm is pulverized in a chilled hammer-mill to obtain the requisite particle size.

A commercially available asphalt containing drilling additive useful with the present invention is sold by Baker Hughes Inteq of Houston, Texas under the trademark BLACK MAGIC SFT.

For those applications of this invention where the additive composition is used as a spotting fluid pill, the relative amounts of asphalt and ester are 46-74% (vol.) ester and 34-55 lb/bbl Black Magic SFT. For those applications of this invention where the additive composition is used as a lubricant in the drilling mud, the relative amounts of asphalt and ester are 0.4-7.4 vol. r and 0.3-5.5

lb/bbl Black Magic SFT.

After reduction to the specified particle size, the asphalt may be blended with the optional additives. Suitable surfactants include zwitterions; anionic surfactants, such as carboxylic acid salts, sulfonic acid salts, sulfuric acid ester salts; phosphoric and polyphosphoric acid esters, and perfluorinated anionics; cationics, such as long-chain amines and their salts, diamines and polyamines and their salts, quaternary ammonium salts, polyoxyethylenated long-chain amines, and amine oxides; and nonionic surfactants such as polyoxyethylenated alkyphenols and alkylphenol ethoxylates, polyoxyethylenated straight-chain alcohols and alcohol ethoxylates, polyoxyethylenated mercaptans, long-chain carboxylic acid esters, alkanolamine "condensates" and alkanolamides, and tertiary acetylenic glycols.

Anticaking and grinding agents such as calcium silicate or diatomaceous earth may also be included in an amount of between about 0.2 and 15 vol. %.

Antigellation agents such as sodium bicarbonate, may also be included in an amount of between about 1 and 4 lb/bbl (with a final volume of 11 lbs/bbl).

Alkalinity control agents such as lime ($Ca(OH_2)_2$) or $Mg(OH)_2$ may be used in an amount of 2% to 40 vol. % to form calcium and other soaps.

To prepare a pill, a mixing pit or tank is preferably cleaned to avoid unnecessary contamination. Clean water is pumped through the mixing manifolds to flush out all the residual drilling mud. Waste water is dumped from the tank and lines. Spotting fluid concentrate and barite or other weighting agent are then mixed in the desired proportions.

When it becomes necessary to release a stuck drill string and time is critical, a spotting fluid pill comprising the aqueous-based concentrate suitably conditioned is prepared. The finished spotting fluid should be pumped down the drill string into the open hole in sufficient quantity to immerse the entire annular interval affected. The pill should be delivered within 1 to 12 hours for best

results. The affected region is typically soaked with the fluid until the pipe is freed. An additional quantity of fluid should be pumped periodically to insure adequate soaking and the string should be worked vertically. Generally, an additional 1/2 to 2 barrels of fluid are pumped per hour, preferably an additional 1/2 to 1 barrel of fluid are pumped, and optimally about 1 barrel is pumped per hour. When the pipe is free, it is pulled up from the problem zone leaving the spotting fluid to lubricate and seal the low pressure sand formation. The drill string is staged back into the hole and the drilling fluid is circulated to incorporate the spotting fluid pill as lubricant on the mud. The mud may be further conditioned with alkalinity control agent, thinner, defoamer and the like as needed.

In another embodiment, the present invention comprises drilling mud preferably incorporating the spotting fluid concentrate in an amount of from about 1 to 10 percent by volume of the drilling mud, generally in an amount of from about 2 to about 5 percent by volume of the drilling mud. As a lubricating fluid, the present invention reduces the prevalence of drill string sticking. To prepare a lubricating fluid, an aqueous emulsion of ester, asphalt and optional additives is formulated. Components concentrations are the same as mentioned previously. The lubricating fluid is blended into the drilling mud, i.e., circulated in the wellbore during drilling.

The present invention is further illustrated by the following examples.

Examples

A series of formulation in accordance with the present invention were made in accordance with Examples 1-4 in Table 1 having densities ranging from 10-16 lbm/gal. The ester selected for the testing was Arizona 2154 and the asphalt was Black Magic SFT. In addition, barite (e.g., MILBAR available from Baker Hughes Inteq), water and bicarbonate were added. Testing indicates that the optimum addition rate for bicarbonate was 1.0 lbm/bbl. Having defined this

optimum concentration, a series of 8.0 + 18.0 lbm/gal spot formulations were hot rolled for 18 hours at 200°C with excellent low temperature gellation suppression and acceptable electrical stability (E.S.) values at 20°C F). The 1.0 lbm/bbl bicarb addition was successfully repeated four (4) times at 200°C. Referring to Table 2, further tests indicated that the bicarbonate should be added before water addition or added to the water before incorporation into the spot. Testing at 270°F and 300°F indicate that temperature accelerates the hydrolysis. The results of Tables 1 and 2 indicate that the drilling fluid additive of this invention can be blended into an acceptably stable invert emulsion.

TABLE 1

Example	1	2	3	4
Density, lbm/gal	10	12	14	16
A-2154, mls	224	217	200	189
SFT, gms	62	56.5	51	45.5
Bicarb, gms	1	7	1	1
Tap water, mls	38.5	24.5	21	10.5
MILBAR, gms	135	240	345	455
Electrical Stability (E.S.) Meter, Model "D"				
Initial	275	390	430	470
After 18 hour 200°F hot roll	270	520	520	500

All samples remained fluid after cool down to 76°F

TABLE 2

Test for order of bicarb addition

A. A-2154...SFT...Bicarb...stir 5 minutes...water...barite

B. A-2154...SFT...mix 5 minutes...water...bicarb...barite

C. A-2154..SFT...mix 5 minutes..water w/bicarb...barite

* bicarb w/water = 14.3 gms per 350 mls.

* 12.0 lbm/gal formulations

E.S. meter; Model "D"

After 18 hour	A	B	C
200°F hot roll	410	250	420

While preferred embodiments have been shown and described, various modifications and substitutions may be made thereto without departing from the spirit and scope of the invention. Accordingly, it is to be understood that the present invention has been described by way of illustrations and not limitation.

What is claimed is:

CLAIMS

CLAIM 1. A spotting fluid composition suitable for use in downhole drilling operations in a pill for releasing periodically stuck drill string or casing comprising:

(a) an ester; and

(b) a particulate asphalt material combined with said ester in an amount effective to release periodically stuck drillstring or casing.

CLAIM 2. The composition of claim 1 wherein:

said ester comprises monohydric alcohol esters of fatty acids.

CLAIM 3. The composition of claim 2 wherein said ester further comprises:

the 2-ethylhexanol ester of tall oil fatty acid.

CLAIM 4. The composition of claim 1 wherein said asphalt comprises:

particulate asphalt having an ASTM D-36 softening point of at least 290°F, an ASTM D-5 penetration depth not exceeding about 5 mm, and a particulate size not exceeding more than about 2 percent retained on a 40 mesh U.S. screen.

CLAIM 5. The composition of claim 1 wherein said asphalt comprises:

a naturally occurring asphalt or asphaltite.

CLAIM 6. The composition of claim 1 in which said ester comprises an oil soluble ester which is pumpable at room temperature.

CLAIM 7. The composition of claim 6 wherein:

said ester further comprises one or more liquid esters made from C_1-C_{10} alcohol esters of C_{12}-C_{22} saturated and unsaturated fatty acids.

CLAIM 8. The composition of claim 6 wherein said ester is selected from the group consisting of:

methyl, ethyl, proply, butyl, pentyl, hexyl, heptyl, 2-EH or isooctyl caproate, caprylate, laurate, myristic, palmitate, stearate, oleate, erucate or mixtures thereof.

CLAIM 9. The composition of claim 1 including at least one of the additives selected from the group consisting of surfactants, alkilinity control agents, anticaking agents, grinding agents, water or aqueous solutions, suspension agents and antigelling agents.

CLAIM 10. An improved method of releasing a stuck drill string in the borehole of an underground formation during drilling operations employing an aqueous drilling fluid which comprises contacting said stuck drill string with an additive composition effective to reduce the annular pressure exerted by the drilling fluid against the stuck drill string and to release said stuck drill string, said additive composition comprising:

(a) an ester

(b) a particulate asphalt material combined with said ester in an amount effective to release periodically stuck drillstring or casing.

CLAIM 11. An invert emulsion drilling fluid, comprising:

(a) an aqueous medium,

(b) from about 1 to about 10 volume percent of the drilling fluid additive composition of claim 1.

CLAIM 12. A method of preventing sticking of tubular equipment in the wellbore of a subterranean well in the drilling, completion, or workover of such well, comprising the steps of:

(a) preparing a water-based drilling fluid;

(b) adding to the water-based drilling fluid the additive of claim 1; and

(c) circulating the drilling fluid into, through, and out of the tubular equipment into the subterranean well, whereby the drilling fluid contacts the bore hole wall of the well.

CLAIM 13. The method of claim 12 further comprising the step of conducting operations involving movement of tubular equipment in the bore hole of said well.

CLAIM 14. A drilling fluid additive comprising:

(a) an ester; and

(b) a particulate asphalt material combined with said ester.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 E21B31/03 C09K7/00 C09K7/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C09K E21B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP,A,0 324 887 (HENKEL) 26 July 1989 see page 3, line 14 - page 4, line 17 see page 5, line 15 - line 40 ---	1-14
Y	US,A,5 120 708 (S.MELEAR) 9 June 1992 see column 4, line 9 - line 68 see column 7, line 1 - column 8, line 16 ---	1-14
Y	US,A,3 709 819 (W.C.BROWNING) 9 January 1973 see column 3, line 3 - line 63 see claims 1-5 ---	1,4,11, 14
Y	US,A,2 773 670 (G.MILLER) 11 December 1956 see column 1, line 46 - line 70 see claims 1-10 -----	1,5,11, 14

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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